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(54) PROCESS FOR THE MANUFACTURE OF WATER-REPELLENCY AGENTS

(71) We, WACKER-CHEMIE G.m.b.H., a body corporate organized according to the laws of Germany, of Postfach, Prinzregentenstrasse 22, 8 Munchen 22, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

In water-repellency agents for mouldings and coatings made from compositions containing inorganic binders or compositions consisting of such binders it is necessary to distinguish between those agents that are applied to the surface of the mouldings or coatings and those agents that are added to the compositions containing or consisting of inorganic binders before the composition is shaped. The present invention relates to a process for the manufacture of water-repellency agents of the latter kind.

Mixing compositions containing or consisting of inorganic binders with water-repellency agents before shaping has the advantage, compared with the application of water-repellency agents to the finished mouldings or coatings, that it allows the manufacture of mouldings and coatings, which are water-repellent not only on their surface but also in all parts of their interior. This has, for example, a very favourable effect if cracks subsequently arise. It has the additional advantage that it requires considerably less expenditure of labour.

The water-repellency agents hitherto proposed for addition to compositions containing or consisting of inorganic binders before shaping, include aqueous emulsions of organopolysiloxanes, aqueous pastes consisting of reaction products of organohalogenosilanes with aqueous hydrated lime, powders which are manufactured by hydrolysis of organotrichlorosilanes, and metal salts of higher fatty acids.

The aqueous emulsions of organopolysiloxanes and the pastes of the type described above suffer from the disadvantages that they can only be added to the compositions immediately before use of the compositions, and that because of their water content they require a high expenditure on storage and transport. The addition of the water-repellency agents to the compositions immediately before use of the compositions introduces the possibility of several defects and especially that uniform mixing of the compositions with the water-repellency agent is difficult and is frequently not obtained.

Because of their low wettability it is also difficult uniformly to distribute powders which are manufactured by hydrolysis of organotrichlorosilanes, in the compositions simultaneously with or after the addition of water, and the water-repellency achieved by these powders is therefore frequently low.

In the case of metal salts of higher fatty acids it is frequently observed that before or after the shaping of compositions containing inorganic binders and water they will float on the surface of the compositions and are no longer uniformly distributed in these compositions. Further, these soaps are degraded in a relatively short time through weathering influences and/or biologically, and thereby become inactive.

In contrast, the process of the invention provides pulverulent water-repellency agents which are free from all the disadvantages described above, that is to say, they can already be added to the compositions containing or consisting of inorganic binders, or to the additives for such compositions, for example pigments, long before the final application of these compositions or, if desired, they can easily be uniformly distributed in the compositions containing inorganic binders shortly before, simultaneously with or after the addition of water, without demixing occurring, and they permit the manufacture of mouldings and coatings which possess a more powerful water-repellency than mouldings and coatings of compositions containing inorganic binders

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which have before shaping been mixed with water-repellency agents hitherto known, for example finely granular methylpolysiloxane. The water-repellency agents manufactured in accordance with the invention furthermore have the advantage compared to, for example, finely granular methylpolysiloxane that they are more easily obtainable.

The subject of the invention is a process for the manufacture of water-repellency agents wherein quicklime is slaked with an aqueous emulsion of at least one organopolysiloxane which on average contains 0.8 to 1.8 SiC-bonded hydrocarbon radicals per silicon atom, and the products thus obtained, if they are not already pulverulent, are dried and, if necessary, ground.

It is to be assumed that the water-repellency agents manufactured according to the invention contain free lime, whilst on reaction of hydrated lime, with organohalogeno - silanes the free lime is neutralised. Since, however, it has hitherto been assumed, for example on the basis of German Patent Specification 1,065,551, that free lime impairs the action of organosilicon compounds in conferring water-repellency, the effectiveness of the water-repellency agents manufactured according to the invention is extremely surprising.

The quicklime (CaO) sometimes also described as "burnt lime" or "calcium oxide", can be used in the form of lime lumps or of finely divided lime. In order to facilitate the mixing of the organopolysiloxane emulsion with the quicklime, and since an especially finely divided water-repellency agent is thereby obtained, the use of finely divided lime, that is to say of pulverulent quicklime, is preferred.

The SiC-bonded hydrocarbon radicals in the organopolysiloxanes in the aqueous emulsions used in accordance with the invention may be alkyl, alkenyl, cycloalkyl, cycloalkenyl, aryl, aralkyl or alkaryl radicals. They are preferably alkyl radicals with 1 to 16 carbon atoms, for example, methyl, ethyl, n - propyl, isopropyl or n - butyl radicals, especially methyl radicals, or phenyl radicals. In addition to the SiC-bonded hydrocarbon radicals (and, naturally, siloxane oxygen atoms) the organopolysiloxanes used in the process according to the invention may contain an average of up to 1.25 Si-bonded hydrogen atoms and/or an average of up to 1.7 Si-bonded hydroxyl groups and/or an average of up to 1.7 Si-bonded alkoxy groups with 1 to 4 carbon atoms, especially methoxy or ethoxy groups, per silicon atom. Mixtures of different organopolysiloxanes can be used. It is one of the advantages of the process according to the invention that it is possible to use in the process, as organopolysiloxanes, hydrolysis products of the products, boiling above 70°C, especially between 100°C and 150°C, in each case at or at about 760 mm Hg (absolute), of the reaction of methyl chloride with silicon in the direct synthesis of methylchlorosilanes according to Rochow. Such a synthesis is described in detail in, for example, Specification No. 575667 and the products thereof boiling above 70°C are discussed in detail in Specification No. 714461. The viscosity of the organopolysiloxanes which are employed for the preparation of the aqueous emulsions used in accordance with the invention should appropriately not exceed 1000 cSt, measured in a 50% strength by weight toluene solution at 25°C.

The organopolysiloxanes are preferably employed in amounts of 10 to 150% by weight relative to the weight of the quicklime.

The manufacture of emulsions of organopolysiloxanes in water is generally known and the manufacture of the emulsions used in accordance with the invention can take place according to these known processes. Many aqueous emulsions of organopolysiloxanes, containing an average of 0.8 to 1.8 SiC-bonded hydrocarbon residues per silicon atom, that is to say emulsions which can be employed in the process according to the invention, are commercially available.

The dispersing agents usually employed for the manufacture of aqueous emulsions of organopolysiloxanes can also be employed in the preparation of the organopolysiloxane emulsions used in accordance with the invention. Examples of such dispersing agents are protective colloids, for example polyvinyl alcohol, which may optionally still contain up to 40 mol % of acyl groups, for example acetyl groups or acyl groups derived from so-called Koch acids, gelatine and cellulose derivatives, for example water-soluble methylcellulose; anionic emulsifiers, for example, alkali metal salts or ammonium salts of long-chain fatty acids, of organic sulphonic acids or of acid sulphuric acid esters for example sodium laurate. sodium oleate, sodium iso - propyl - naphthalenesulphonate, sodium di - octylsulphosuccinate, triethanolammonium oleate and sodium lauryl sulphate; cationic emulsifiers, for example, stearyl ammonium chloride, and non-ionic emulsifiers, for example, sorbitol monolaurate, polyoxy - ethylene ethers of monohydric or polyhydric aliphatic alcohols or alkylphenols, and block copolymers of blocks of dimethylpolysiloxanes and polyethylene glycols joined by an SiOC-bond. Mixtures of different dispersing agents can be employed. The dispersing agents are appropriately employed in amounts of 0.1 to 5% by weight relative to the weight of the organopolysiloxanes.

For the preparation of the organopolysiloxane emulsions used in accordance with the invention, the organopolysiloxane can be employed in a solvent-free form or in the form of a solution in an organic solvent which is

liquid under normal conditions (760 mm Hg absolute/20°C). Preferably, such solutions are employed for the preparation of the emulsions used in accordance with the invention. Examples of suitable solvents are aliphatic hydrocarbons, for example, alkanes having boiling points in the range of 120°C to 180° C at 760 mm Hg (absolute); aromatic hydrocarbons, for example, toluene, xylenes and trimethylbenzenes; chlorinated hydrocarbons, for example, trichloroethylene; alcohols, for example, isopropyl alcohol and diacetone alcohol; esters, for example, ethyl acetate; ethers, for example, di - n - butyl ether; and ketones, for example, methyl ethyl ketone. Mixtures of different solvents can be used. The organic solvents are preferably used in amounts of 25 to 100% by weight relative to the weight of the organopolysiloxanes.

The proportion of water in the emulsion is not a decisive factor. It is merely necessary to ensure that on slaking the lime in the presence of the organopolysiloxanes, at least 1 mol of water is present per mol of CaO, since otherwise the quicklime is not completely slaked. The upper limit of water which is imposed merely by economic considerations and which is therefore preferred is that which leads to a composition consisting of lime slaked with the organopolysiloxane emulsion which contains 10% by weight of free water. If more water is used, insufficient water evaporates through the heat of hydration and/or insufficient water is bonded as water of hydration. It is then necessary to remove at least the amount of free water which exceeds 10% by weight of the composition obtained after slaking, by drying, which may include the addition of known dehydrating agents such as silica gel, to the slaked lime, and where appropriate to grind the product obtained after drying in order to obtain the desired powder.

The water-repellency agents according to the invention are preferably used in amounts of 0.1 to 2.0% by weight, especially 0.5 to 1.0% by weight, in each case relative to the dry weight of the compositions containing or consisting of inorganic binders.

As examples of compositions containing or consisting of inorganic binders, to which the water-repellency agents manufactured according to the invention can be added, there may be mentioned: compositions based on lime CaO), or $Ca(OH)_2$), for example lime mortar and lime paints, Portland cement, finishing plaster and waterglass paints, for example distempers. These compositions may contain conventional adjuvants and additives, for example, sand, vermiculite (expanded mica), perlite (expanded lava), fine gravel, wood flour, wood shavings, asbestos, setting retarders, gluconic acid, calcium gluconate, vinyl polymers and pigments, for example oxide colours.

If compositions containing water-repellency agents manufactured according to the invention and inorganic binders are used for the manufacture of coatings, then the coatings can be applied to the substrates by casting, spraying or spreading.

The illustrative Examples which follow show that the water-repellency agents manufactured according to the invention are surprisingly outstandingly active without the conjoint use of the known substances which neutralise the action of free lime on organosilicon compounds. It is possible, however, that even better results, can be achieved by the conjoint use of substances which neutralise the action of free lime on organosilicon compounds, such as vinyl resins, including polymethyl methacrylate, chlorinated rubber and magnesium carbonate.

Example 1

(I) The reaction products of methyl chloride with silicon, boiling between 100°C and 150° C at 760 mm Hg (absolute), obtained in the direct synthesis of methylchlorosilanes according to Rochow, are poured into water. A solution in toluene containing 75% by weight of organopolysiloxanes is manufactured from the oily phase thereby obtained. An emulsion is manufactured from 400 g of this solution, 40 g of a 10% strength by weight aqueous solution of polyvinyl alcohol containing residual acetyl groups (saponification number, that is to say milligrams of KOH, required for splitting off and neutralising the remaining acetyl groups in 1 g of polyvinyl alcohol: 140; viscosity, measured in 4% strength by weight aqueous solution at 20°C: 25cP) and 160 g of water. 65 g of water are first added to 420 g of the emulsion thus obtained, containing 50% by weight of organopolysiloxanes, and 420 g of pulverulent quicklime are then added whilst stirring. 840 g of a powder containing 25% by weight of organopolysiloxane and 2.6% by weight of free water are obtained.

(IIa) a plaster consisting of a mixture of 2 parts by weight of white lime (compare DIN Regulation 1060, draft of June 1952), 1 part by weight of white Portland cement, 8.5 parts by weight of sand of at most 1.5 mm particle size and 0.5 parts by weight of red iron oxide is mixed with 1% by weight, relative to its weight, of the pulverulent water-repellency agent of which the manufacture has been described above under (I). A plastic mortar which can be worked with a bricklayer's trowel is produced by adding 1 part by weight of water to 6 parts by weight of the mixture thus obtained in the course of which no flotation of the water-repellency agent can be observed. Discs (A) are shaped from this mortar with the aid of a glass ring (internal diameter: 10 cm. height 2 cm.).

(IIb) For the purpose of comparison, the procedure described above under (IIa) is repeated with the modification that in place of 1% by weight of the water-repellency agent of which the manufacture has been described above under (I), 0.25% by weight of pulverulent methylpolysiloxane manufactured by hydrolysis of methyltrichlorosilone are used. Discs (B) are obtained.

Because the water-repellency agent of which the manufacture has been described above under (I) only contains 25% by weight of organopolysiloxane, the discs (B) contain the same amount of organopolysiloxane as the discs (A).

(IIc) For further comparison, the procedure described under (IIa) is repeated with the modification that no water-repellency agent is conjointly used. Discs (C) are obtained.

8 days after carrying out procedures (IIa), (IIb) and (IIc) the discs are weighed and then stored for 90 minutes under water at 20°C in such a way that the surface of the water is 20 mm above the discs. The discs are then taken out of the water and again weighed after draining. The water absorption on storage in water as described above, that is to say the weight increase in % relative to the weight of the dry discs is given in Table I below:

Table I

Discs	Water absorption in % by weight
A	0.17
B	14.2
C	17.2

EXAMPLE 2

(a) The reaction products of methyl chloride with silicon in the direct synthesis according to Rochow, boiling between 100 and 150°C at 760 mm Hg (absolute), are poured into water. A solution in toluene containing 75% by weight of organopolysiloxanes is manufactured from the oily phase thereby obtained. An emulsion containing 50% by weight of organopolysiloxanes is manufactured from 2000 g of this solution, 200 g of a 10% strength by weight solution of polyvinyl alcohol of the nature described in Example 1 and 800 g of water.

(b) The procedure described above under (a) is repeated with the modification that in place of 800 g of water in the preparation of the emulsion, 1800 g of water are used. The emulsion (b) thus obtained accordingly contains 37.5% by weight of organopolysiloxanes.

(c) The procedure described under (a) is repeated with the modification that in place of 800 g of water 3800 g of water are used. The emulsion (c) thus obtained accordingly contains 25% by weight of organopolysiloxanes.

100 g of water are initially added to 1600 g each of emulsions (a), (b) and (c), and 1200 g of pulverulent quicklime are added thereto whilst stirring. Powders are hereupon obtained in each case.

Samples of plaster of the type described in Example 1 under (IIa) are in each case mixed with 1% by weight, relative to their weight, of the water-repellency agent manufactured as described above, treated with water as described in Example 1 under (IIa) and shaped into discs. After 5 days the water absorption of the discs is determined as described in Example 1. The results of this determination are given in Table II:

Table II

Water-repellency agent manufactured using emulsion	Water absorption in % by weight
a	0.7
b	3.1
c	8.2

EXAMPLE 3

(I) A mixture of 15 litres of water and 15 litres of ethanol is added over the course of 3 hours to a mixture of 150 kg of methyltriethoxysilane and 100 ml of concentrated hydrochloric acid heated to boiling under reflux. After distilling off the constituents of the reaction mixture boiling up to 100°C at 760 mm Hg (absolute) a methylpolysiloxane with ethoxy groups, having a viscosity of 15 to 25 cSt/25°C, is obtained. A solution in toluene containing 75% by weight of organopolysiloxanes is manufactured from 60 parts by weight of this methylpolysiloxane and 15 parts by weight of a dimethylpolysiloxane having a viscosity of 350 cSt/25°C. The procedure described in Example 1 under (I) is repeated with the modification that this solution is used in place of the solution described in Example 1.

(IIa) Plaster of the type described in Example 1 under (IIa) is mixed with 1% by weight, relative to its weight of the pulverulent water-repellency agent, the manufacture of which has been described above under (I), as described in Example 1 under (IIa), treated with water and shaped into discs (A).

(IIb) For comparison, the procedures described above under (IIa) is repeated with the modification that no water-repellency agent is conjointly used. Discs (B) are obtained.

14 days after carrying out the procedures (IIa) and (IIb) the water absorption of the discs is determined as described in Example 1. The results of this determination are given in Table III.

Table III

Discs	Water absorption in % by weight
(A)	2.8
(B)	20.3

EXAMPLE 4

(a) An additive mixture containing pigments as the essential constituent and consisting of the following pulverulent constituents: 45 parts by weight of dolomite, 15 parts by weight of titanium dioxide, 32 parts by weight of barite, 4 parts by weight of red iron oxide and 4 parts by weight of yellow iron oxide is first mixed with 0.2% by weight, relative to its weight, of the pulverulent water-repellency agent of which the manufacture has been described in Example 1 under (I), and then with 125% by weight relative to its weight, of a 25% strength by weight aqueous solution of potassium waterglass (molar ratio of SiO_2: K_2O=3.8). The waterglass paint thus obtained is coated onto a concrete sheet (coating a).

(b) For comparison, the procedure described above under (a) is repeated with the modification that instead of the 0.2% by weight of the water-repellency agent of which the manufacture has been described in Example 1 under (I), 1% by weight of a pulverulent product containing 25% by weight of organopolysiloxanes is used, this product having been obtained by pouring the reaction products of methyl chloride with silicon in the direct synthesis according to Rochow, boiling between 100 and 150°C at 760 mm Hg (absolute), into a suspension of mica powder and removing the water and the hydrogen chloride from the mixture thereby obtained. (Coating B).

(c) For a further comparison, the procedure described under (a) is repeated with the modification that no water-repellency agent is conjointly used. (Coating C).

One day after carrying out procedure (a), (b) and (c), 0.5 ml of water are dripped onto the surface of the coatings in each case, and the time in seconds until the water has disappeared or been absorbed by the coatings is determined. The following results are obtained:

Table IV

Coating	Seconds
a	2460
b	1080
c	184

It has surprisingly also been found that compositions containing or consisting of inorganic binders, based on lime, especially lime mortar and lime plaster and Portland cement, which can of course also contain the conventional adjuvants and additives already mentioned above, as a result of containing the water-repellency agents manufactured according to the invention yield mouldings and coatings with a particularly high air pore content, coupled with high water repellency, despite the known properties of silicones of preventing the formation of foam. As a result of this air pore content the mouldings and coatings have a particularly low specific gravity and are elastic, less prone to crack formation and especially good heat insulators.

The pore content and pore size can be regulated by varying the amount of the water-repellency agent according to the invention.

EXAMPLE 5

Samples of mortar consisting of a mixture of 2 parts by weight of hydrated white lime, 1 part by weight of Portland cement PZ 275), 8 parts by weight of sand having a particle size of 0.3 mm and 0.1 part by weight of red iron oxide are mixed with the amounts specified in Table V of the pulverulent water-repellency agent of which the manufacture has been described in Example 1 under (I).

Pourable plaster mortars are prepared in a laboratory mortar mixer by adding 0.25 parts by weight of water to 1 part by weight of the mixture described above.

The air pore content of the plaster mortar samples was determined with the aid of an air pore testing instrument, type "Air Content Tester for Concrete", of Messrs. Weissgerber, Frankfurt/Main. The Table V shows the results of the measurements.

Table V

Additive in % by weight relative to the dry weight of the mortar	Air pore content in % by volume
0	0.9
0.2	4.1
0.5	17.0
1.0	22.0

WHAT WE CLAIM IS:—

1. A process for the manufacture of water repellency agents, which comprises slaking quicklime with an aqueous emulsion of an organopolysiloxane containing an average of from 0.8 to 1.8 SiC-bonded hydrocarbon radicals per silicon atom at least one mol of water being used per mol of quicklime, and, if the product is not already pulverulent, drying and, if necessary, grinding the product.

2. A process as claimed in claim 1, wherein the quicklime is used in pulverulent form.

3. A process as claimed in claim 1 or claim 2, wherein the SiC-bonded hydrocarbon radicals are alkyl radicals containing 1 to 16 carbon atoms and/or are phenyl radicals.

4. A process as claimed in claim 3, wherein the SiC-bonded hydrocarbon radicals are methyl radicals and/or phenyl radicals.

5. A process as claimed in any one of claims 1 to 4, wherein the organopolysiloxanes

containing an average of up to 1.25 Si-bonded hydrogen atoms per silicon atom.

6. A process as claimed in any one of claims 1 to 5, wherein the organopolysiloxanes contain an average of up to 1.7 Si-bonded hydroxyl groups per silicon atom.

7. A process as claimed in any one of claims 1 to 6, wherein the organopolysiloxanes contain an average of up to 1.7 Si-bonded alkoxy groups with 1 to 4 carbon atoms per silicon atom.

8. A process as claimed in claim 7, wherein the alkoxy groups are methoxy or ethoxy groups.

9. A process as claimed in claim 1 or claim 2, wherein the organopolysiloxane is the hydrolysis product of the product boiling above 70°C at 760 mm Hg of the reaction of methyl chloride with silicon in the direct synthesis of methylchlorosilanes according to Rochow.

10. A process as claimed in claim 9, wherein the boiling point of the product of the reaction of methyl chloride with silicon is between 100°C and 150°C.

11. A process as claimed in any one of claims 1 to 10, wherein the viscosity of the organopolysiloxane does not exceed 1000 cSt, measured in a 50% by weight toluene solution at 25°C.

12. A process as claimed in any one of claims 1 to 11, wherein the organopoly - siloxane is used in an amount of from 10 to 150% by weight, relative to the weight of the quicklime.

13. A process as claimed in any one of claims 1 to 12, wherein the aqueous emulsion also contains at least one dispersing agent.

14. A process as claimed in claim 13, wherein the dispersing agent is a protective colloid or an anionic, cationic or non-ionic emulsifier.

15. A process as claimed in claim 13 or claim 14, wherein the dispersing agent is present in an amount within the range of from 0.1 to 5% by weight relative to the weight of the organopolysiloxane.

16. A process as claimed in any one of claims 1 to 15, wherein the organopolysiloxane emulsion is prepared by emulsifying a solution of the organopolysiloxane in a liquid organic solvent.

17. A process as claimed in claim 16, wherein the organic solvent is used in an amount of from 25 to 100% by weight relative to the weight of the organopolysiloxane.

18. A process as claimed in claim 16 or claim 17, wherein the solvent is an aliphatic hydrocarbon, an aromatic hydrocarbon, a chlorinated hydrocarbon, an alcohol, an ester, an ether or a ketone.

19. A process as claimed in claim 18, wherein the solvent is an alkane having a boiling point in the range of from 120°C to 180°C at 760 mm Hg, toluene, a xylene, a trimethylbenzene, trichloroethylene, isopropylalcohol, diacetonealcohol, ethyl acetate, di - n - butyl ether or methylethyl ketone.

20. A process as claimed in any one of claims 1 to 19, wherein the amount of water is such that the slaked product consisting of slaked lime and organopolysiloxane contains at most 10% of free water.

21. A process for the manufacture of a water-repellency agent conducted substantially as described in any one of the Examples herein.

22. A water-repellency agent comprising slaked lime and an organopolysiloxane whenever prepared by a process as claimed in any one of claims 1 to 21.

23. A composition containing or consisting of an inorganic binder and a water-repellency agent as claimed in claim 22.

24. A composition as claimed in claim 23, wherein the water-repellency agent is present in an amount of from 0.1 to 2% by weight calculated on the dry weight of the inorganic binder.

25. A composition as claimed in claim 24, wherein the water-repellency agent is present in an amount of from 0.5 to 1% by weight calculated on the dry weight of the inorganic binder.

26. A composition as claimed in any one of claims 23 to 25, wherein the composition is a composition based on lime, Portland cement, finishing plaster or is a waterglass paint.

27. A composition as claimed in claim 26, wherein the composition based on lime is a lime mortar or a lime paint.

28. A composition as claimed in claim 26, wherein the waterglass paint is a distemper.

29. A composition as claimed in any one of claims 23 to 28 which also contains a substance which neutralises the action of free lime on organosilicon compounds.

30. A composition as claimed in claim 29, wherein the said substance is a vinyl resin, chlorinated rubber or magnesium carbonate.

31. A composition as claimed in claim 23, substantially as described in any one of the Examples herein.

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